

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-150179

(43)Date of publication of application : 02.06.1998

(51)Int.Cl.

H01L 27/14  
H01L 27/148  
H01L 31/0232

(21)Application number : 08-307952

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(22)Date of filing : 19.11.1996

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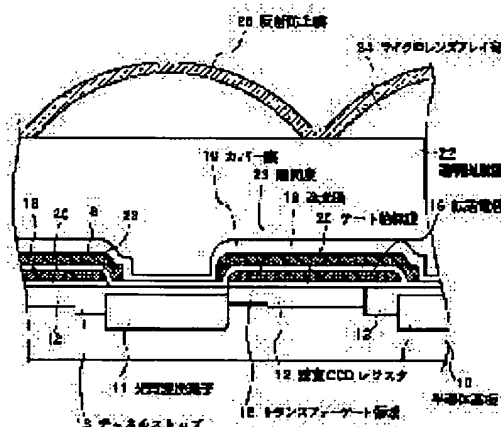
## (54) SOLID-STATE IMAGE SENSING DEVICE

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To realize a solid-state image sensing device which is kept free from flares and ghosts and capable of dispensing with high hermetic sealing by a method wherein a micro lens is provided above a photodetecting part formed on a substrate, and an anti-reflection film of aluminum fluoride is provided onto the surface of the micro lens.

**SOLUTION:** An anti-reflection film 26 of aluminum fluoride is provided to the surface of a microlens array 24. In result, the surface of the micro lens can be more lessened in light reflectivity than a case where an anti-reflection film of magnesium fluoride is provided, so that flares and ghosts can be lessened when the image of an object of high rightness is picked up by an image sensing device of this constitution.

Cryolite is deliquescent but an aluminum fluoride film is not deliquescent, so that special sealing is not required. Furthermore, aluminum fluoride is not soluble in any solvent other than water and little soluble in water, so that an anti-reflection film of aluminum fluoride functions as a protective film for a solid-state image sensing device when it is provided as an anti-reflection film onto the a micro lens.



## LEGAL STATUS

[Date of request for examination] 19.11.1996

[Date of sending the examiner's decision of rejection] 16.03.1999

[Kind of final disposal of application other than the  
examiner's decision of rejection or application  
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of  
rejection] 11-06319

[Date of requesting appeal against examiner's  
decision of rejection] 15.04.1999

[Date of extinction of right]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a solid state camera.

[0002]

[Description of the Prior Art] In order to prevent an echo of an optical lens front face in an optical lens from the former the technique of preparing the antireflection film of a fluorine system content inorganic compound in the transparence resin film upper part was known. As antireflection film of the fluorine system content inorganic compound used for an optical lens, magnesium fluoride, aluminum fluoride, barium fluoride, lithium fluoride, the calcium fluoride, the cryolite, etc. are known (refer to JP,3-242602,A).

[0003] However, all these construction material was not used as an antireflection film prepared in the micro-lens upper part of the solid state camera of a CCD mold, and magnesium fluoride and a cryolite are known as construction material of the antireflection film formed in the micro-lens upper part (refer to JP,4-259256,A). The cross-section structure of the unit pixel of the solid state image pickup device of the conventional CCD mold indicated by the description of this invention is shown in drawing 6.

[0004] In drawing 6, the transfer gate field 35 which reads a charge to the vertical CCD register 32 is formed into the semi-conductor substrate 30 from an optoelectric transducer 31, the vertical CCD register 32, and an optoelectric transducer 31. An insulator layer 40 is formed on the semi-conductor substrate 30, and the transfer electrode 36 is formed on the insulator layer 40 including the upper part of the vertical CCD register 32. A light-shielding film 38 is formed through the phosphorus glass layer 41 on a transfer electrode, the transparence resin layer 42 is formed on a light-shielding film, and the micro-lens array section 44 which consists of a transparence resin layer is further formed on it. Furthermore, the antireflection film 46 which consists of magnesium fluoride or a cryolite is formed in the front face of the micro-lens array section 44. An antireflection film is formed by a vacuum deposition method etc.

[0005] Since an echo of a lens front face was reduced as compared with the case where an antireflection film is not formed on a micro lens by forming the antireflection film by magnesium fluoride or the cryolite in the micro-lens upper part, the flare and the ghost who arise when picturizing a high brightness photographic subject could be reduced to some extent.

[0006]

[Problem(s) to be Solved by the Invention] In the antireflection film of the micro-lens upper part of the conventional solid state camera mentioned above, since magnesium fluoride or a cryolite was used, the following technical problems are produced.

[0007] That is, since the refractive index is larger than the value of the optimal refractive index as an antireflection film determined by the medium of the upper and lower sides of magnesium fluoride when magnesium fluoride is used, an echo is not fully reduced but there is a fault that a ghost cannot fully be controlled as a result.

[0008] The refractive index optimal as an antireflection film is explained to a detail below. Refractive index  $n_1$  An antireflection film is a refractive index  $n_2$ . It is prepared in the micro-lens upper part, and the upper part of an antireflection film is a refractive index  $n_0$ . The case where it is air is considered. Regardless of whenever [ wavelength which carries out incidence /, and incident angle ], at this time, it is the case of  $n_1 = (n_0 n_2)^{1/2}$  that a reflection factor becomes min. Generally the micro lens under an antireflection film consists of a transparence resin layer, and is the refractive index  $n_2$ . It is between 1.35-1.70 at least, and is the refractive index  $n_0$  of air. It is 1. The optimal refractive

index is optically set to 1.16-1.30 from this thing as an antireflection film used for a resin layer. Since the refractive index of magnesium fluoride is 1.38, it is a bigger value than the value of the optimal refractive index optically as an antireflection film, and when it compares with the optimal antireflection film optically, the echo is not fully reduced. [0009] On the other hand, when a cryolite is used, the refractive index is 1.338 and its refractive index is closer to the above-mentioned optimum value than magnesium fluoride. Then, when the antireflection film which consists of a cryolite is prepared in the micro-lens upper part which consists of a transparency resin layer, the reflection factor on the front face of a micro lens is smaller than the case where magnesium fluoride is used as an antireflection film, and can reduce the flare and a ghost further. However, since it has deliquescence, when a cryolite touches the air containing moisture, degradation of the property as an antireflection film of a cryolite is remarkable. Therefore, when using a cryolite for an antireflection film, there is a fault which does not touch the air in which airtightness is highly carried out and a solid state camera contains moisture that a solid state camera must be closed, like.

[0010] Furthermore, when forming the antireflection film which consists of a fluorine system content inorganic compound on a micro lens, a problem peculiar to a semi-conductor arises. That is, the 1st trouble is that may become the cause of leakage current and the yield may fall, when vapor-depositing an antireflection film and a metallic element mixes into silicon. This is because a metallic element makes medium level in the forbidden band of silicon and tends to become a generation-of-carriers-recombination center through this level. From this, it is easy to contribute the direction of a metallic element with deep level to generating of leakage current.

[0011] The level in the forbidden band of silicon of barium, sodium, magnesium, and aluminum is shown in drawing 2. Drawing 2 shows that they are quite deep, even if it compares sodium (sodium is contained in cryolite  $\text{Na}_3[\text{AlF}_6]$ ), barium, and magnesium with the level of the Lynn and boron which are used in the usual silicon process. There is a fault of being easy to become the cause of leakage current generating from this thing when a cryolite, magnesium fluoride, and barium fluoride are used as an antireflection film.

[0012] Since the magnesium fluoride and the cryolite with which the 2nd trouble was used as an antireflection film of the micro-lens upper part from the former melt into the solvent of an acid or alkali, they have the fault that a device cannot be protected from an acid or alkali.

[0013] The object of this invention is to offer the solid state camera which prevents the flare and a ghost, has the property as a protective coat in which airtight high closure is unnecessary and cannot be easily corroded by an acid and alkali, and possesses a pile antireflection film for lowering of the yield by the metallic element in an antireflection film in a lifting.

[0014]

[Means for Solving the Problem] The solid state camera of this invention is characterized by preparing the antireflection film which consists of aluminum fluoride in the micro-lens front face in the solid state camera with which the micro lens was prepared above the light sensing portion formed on the substrate.

[0015] Since the reflection factor of the light on the front face of a micro lens can be reduced rather than the case where magnesium fluoride is prepared as an antireflection film when aluminum fluoride is prepared in the upper part of a micro lens which consists of transparency resin as an antireflection film, the flare and the ghost at the time of a high brightness photographic subject image pick-up can be reduced. Moreover, since aluminum fluoride does not have a deliquescent problem like [ in the case of a cryolite ], it does not need special closure.

[0016] Moreover, the magnesium fluoride and the cryolite which were used from the former as an antireflection film of the micro-lens upper part of the solid state camera of a CCD mold As opposed to not having a property as a protective coat, since it melts into an acid aluminum fluoride It is almost insoluble to solvents other than water, and since it was refractory (solubility 0.5g / 100g (25 degrees C)), when it uses as an antireflection film on a micro lens also to water, it has the property which was excellent also as a protective coat which protects a solid state camera.

[0017] Furthermore, since aluminum is construction material used general-purpose with wiring etc. in the production line of the usual silicon semi-conductor, even when other semiconductor devices are polluted with the metal (aluminum fluoride) used for an antireflection film, processes, such as washing and surface preparation, have the advantage that it can process by washing (for example, Branson washing etc.) usually performed.

[0018] Furthermore, the one where the medium level in the forbidden band generated when a metal mixes in silicon is deeper tends to mediate the migration of a carrier to a conduction band from a valence band, and tends to cause [ of leakage current ] generating. As compared with sodium, magnesium, and barium, the depth of the level of the forbidden band of aluminum is shallow almost to the same extent as the depth of the level of Lynn or boron. Even when the

direction of aluminum fluoride mixes as a metal atom or ion into silicon by the time of antireflection film vacuum evaporation etc. and is spread, it is hard to become a generation-of-carriers-recombination center and hard to become the cause of leakage current generating rather than magnesium fluoride, barium fluoride, and a cryolite from this.

[0019]

[Embodiment of the Invention] Next, the gestalt of operation of this invention is explained to a detail with reference to a drawing. Drawing 1 shows the typical partly sectional fragmentary schematic illustration for explaining the gestalt of operation of the solid state camera of this invention.

[0020] At the solid state camera of this invention, the channel stop 13 established in the transfer gate field 15 which reads a charge, and the optoelectric-transducer 11 upper part is established in the semi-conductor substrate 10 at the vertical CCD register 12 from the optoelectric transducer 11, the vertical CCD register 12, and the optoelectric transducer 11. Furthermore, gate dielectric film 20 is formed on the semi-conductor substrate 10, and the transfer electrode 16 is formed on gate dielectric film 20 including the upper part of the vertical CCD register 12. A light-shielding film 18 is formed through an interlayer film 23 on a transfer electrode, the covering film 19 is formed on a light-shielding film and an interlayer film, the transparence resin layer 22 is formed on the covering film, and the micro-lens array section 24 is further formed on the transparence resin layer 22. A tungsten and aluminum can be considered as construction material used for a light-shielding film 18. The following construction material can be considered as construction material used for the transparence resin layer 22 and the micro-lens array section 24.

- Phenol novolak system POJIREJISUTO for i line or g line photolithography (about 1.68 refractive index)

- The resist for deep UV photolithography (about 1.5 refractive index)

- The resist for electron beam lithography (about 1.5 refractive index)

- The water-soluble resist which consists of casein or gelatin (refractive indexes 1.5-1.6).

[0021] The antireflection film 26 which consists of aluminum fluoride is formed in the upper part of the micro-lens array section 24. The refractive index of aluminum fluoride is 1.35. An antireflection film 26 is formed with a vacuum deposition method etc. In order to enlarge effectiveness as an antireflection film over the incident light of the light (from the wavelength of 350nm to 800nm), it is desirable for main wavelength (wavelength which hits the die length of  $d/(4n)$  to the antireflection film of a refractive index  $n$  and Thickness  $d$ ) to be from 350 to 800nm. As compared with the light of other wavelength regions, the light of main wavelength has the highest reduction effectiveness of the reflection factor by preparing an antireflection film. If this condition is converted into the thickness of aluminum fluoride, it will be set to 64.8 to 148nm.

[0022]

[Example] Below, one example is explained further at a detail. In this example, the transparence resin layer 22 and the micro-lens array section 24 were made into the refractive index 1.68, and the antireflection film 26 which consists of aluminum fluoride was formed so that it might become 102nm (main wavelength of 550nm) of thickness. An antireflection film 26 is formed with a vacuum deposition method etc.

[0023] Next, reducing the reflection factor further as compared with the antireflection film which consists of magnesium fluoride in which the antireflection film which consists of aluminum fluoride shown in the example has the main wavelength of the same thickness is shown.

[0024] The antireflection film of uniform thickness is prepared on the flat ingredient of a refractive index 1.68, and drawing 3, drawing 4, and drawing 5 show the simulation result about the incident angle dependency of a reflection factor in case light (the wavelength of 400nm, 550nm, and 700nm) carries out incidence from the upper part and reflects by the antireflection film interface to the structure which has the medium of a refractive index 1 in the upper part further. About the effectiveness of interference, only the phase contrast produced within an antireflection film is taken into consideration, and it is assumed that it does not depend for a refractive index on wavelength. The thickness of magnesium fluoride is setting thickness of 99.6nm and aluminum fluoride to 101.8nm so that main wavelength may be set [ as opposed to / both / both construction material ] to 550nm.

[0025] The reflection factor at the time of carrying out incidence of the light (the wavelength of 400nm, 550nm, and 700nm) at the include angle of 0 times to 30 degrees is understood that the direction in the case of being aluminum fluoride is lower than the case where an antireflection film is magnesium fluoride from drawing 3, drawing 4, and drawing 5.

[0026] In drawing 3, drawing 4, and drawing 5, the incident angle dependency of the reflection factor by incident light (400nm, 550nm, and 700nm) was indicated. If the wavelength of incident light becomes a light region (from

350nm to 800nm) at least, also in which [ of 0 times to 30 degrees ] incident angle, as for a reflection factor, the direction in the case of being aluminum fluoride will become low from the case where an antireflection film is magnesium fluoride.

[0027] Moreover, in drawing 3 , drawing 4 , and drawing 5 , although the simulation result of the incident angle dependency of a reflection factor at the time of preparing the antireflection film of thickness with which main wavelength is set to 550nm was indicated, as for a reflection factor, the direction if main wavelength is within the limit of at least 350nm - 800nm, in case the thickness of an antireflection film is aluminum fluoride from the case where an antireflection film is magnesium fluoride also in which [ of 0 times to 30 degrees ] incident angle becomes low.

[0028] Moreover, although the simulation result only in case the refractive index of the transparence resin film is 1.68 was indicated, when an antireflection film is prepared on the transparence resin film with 1.35 or more refractive indexes, in the incident angle of 0 times to 30 degrees, as for a reflection factor, the direction in the case of being aluminum fluoride becomes low from the case where an antireflection film is magnesium fluoride.

[0029] In addition, in drawing 3 - drawing 5 , although there is the range of the changed incident angle from 0 times to 30 degrees, it exceeds 30 degrees and, as for a reflection factor, the direction in the case of being aluminum fluoride becomes low from the case where an antireflection film is magnesium fluoride, also in the incident angle of 35 or less degrees.

[0030] By the above, as compared with the case where magnesium fluoride is used as an antireflection film, the direction which used aluminum fluoride as an antireflection film can reduce an echo of a micro-lens front face, therefore can improve a ghost and the flare further. Furthermore, in order for the permeability in a micro-lens front face to also improve, sensibility also improves.

[0031] Furthermore, since a part of light which carried out incidence to the micro lens reflects multiply between between the front face of a micro lens, and a light-shielding film front face or a micro-lens front face, and the silicon front face on a photodiode etc. Although it becomes the factor which the component of the oblique-incidence light to a photodiode increases [ factor ], and worsens a smear From the case where the light which goes to a micro-lens front face uses magnesium fluoride as an antireflection film also about the reflection factor at the time of reflecting on a micro-lens front face from a light-shielding film front face or a silicon front face, in order that the direction which used aluminum fluoride may decrease, a smear is also improved.

[0032] Since it does not have deliquescence like a cryolite, aluminum fluoride can be used satisfactory, even if it does not use special closure.

[0033] Furthermore, aluminum fluoride is hardly dissolved to an acid and alkali. On the other hand, magnesium fluoride dissolves in a nitric acid. Barium fluoride is "the chemistry handbook basic volume I, the edited by Chemical Society of Japan, and 115-118 pages" dissolved in an acid, sal-ammoniac water, etc. From this thing, aluminum fluoride also has the property as a protective coat over an acid and alkali with it.

[0034] Furthermore, the one where the defective level in the forbidden band generated when a metal mixes in silicon is deeper tends to cause [ of leakage current ] generating that it is easy to mediate the migration of a carrier to a conduction band from a valence band. Even when a metal atom or ion mixes and the direction of aluminum fluoride is spread in silicon in the time of antireflection film vacuum evaporatio~~no~~ etc. as compared with barium fluoride, magnesium fluoride, and a cryolite, since it is hard to become a generation-of-carriers-recombination center, there are few possibilities of becoming the cause of leakage current generating.

[0035]

[Effect of the Invention] As explained above, since the antireflection film of the micro-lens upper part was formed by aluminum fluoride in the solid state camera of this invention, sensibility improves and the flare and a ghost decrease. Furthermore, it is effective in the aggravation factor of the smear which a part of light which carried out incidence to the micro lens produces by reflecting multiply between between the front face of a micro lens and a light-shielding film front face or a micro-lens front face, and the silicon front face on a photodiode being improvable by reducing this multiple echo.

[0036] Furthermore, since aluminum fluoride is insoluble to a solvent, and is refractory also to water to it, and hardly has deliquescence in it and it can be used satisfactory in the usual air ambient atmosphere as an antireflection film on a micro lens Excel also as a protective coat which protects a solid state camera, and from the level in the forbidden band of silicon being still shallower It is effective in being hard to become the cause of leakage current generating, and further aluminum from it being the construction material used general-purpose in the production line of a silicon semi-

conductor Also when other semiconductor devices should be polluted, processes, such as washing and surface treatment, are effective in the ability to process by the usual washing approach.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the typical partly sectional fragmentary schematic illustration showing the gestalt of one operation of the solid state camera of this invention.

[Drawing 2] It is the explanatory view showing the medium level of the boron in the forbidden band of silicon, Lynn, sodium, magnesium, barium, and aluminum.

[Drawing 3] It is a diagram to show the effectiveness of the antireflection film of this invention.

[Drawing 4] It is the same diagram as drawing 3 .

[Drawing 5] It is the same diagram as drawing 3 .

[Drawing 6] It is the cross-section schematic drawing showing the solid state image pickup device by the Prior art.

[Description of Notations]

10 30 Semi-conductor substrate

11 31 Optoelectric transducer

12 32 Vertical CCD register

13 Channel Stop

15 35 Transfer gate field

16 36 Transfer electrode

18 38 Light-shielding film

19 Covering Film

20 Gate Dielectric Film

22 42 Transparence resin layer

23 Interlayer Film

24 44 Micro-lens array section

26 46 Antireflection film

40 Insulator Layer

41 Phosphorus Glass Layer

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[Translation done.]



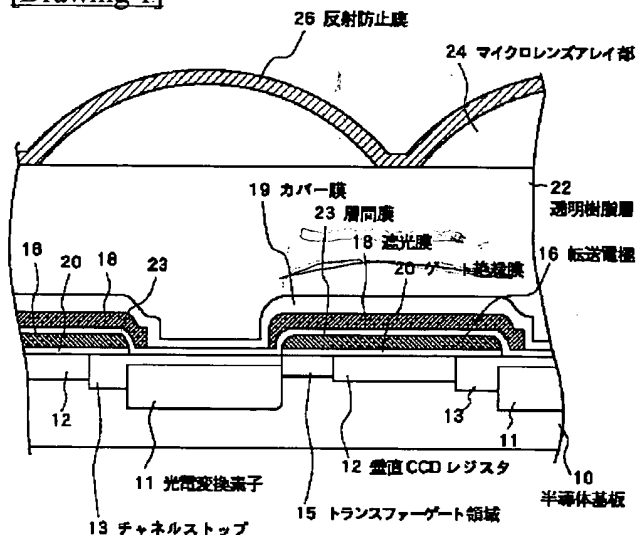
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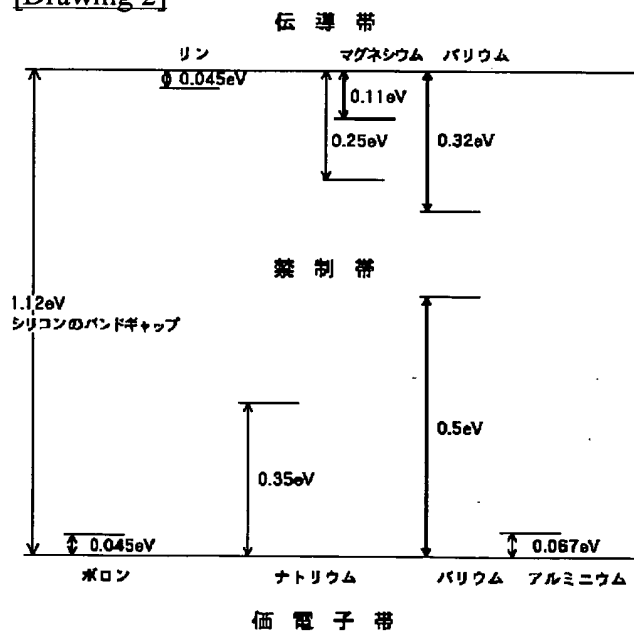
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## DRAWINGS

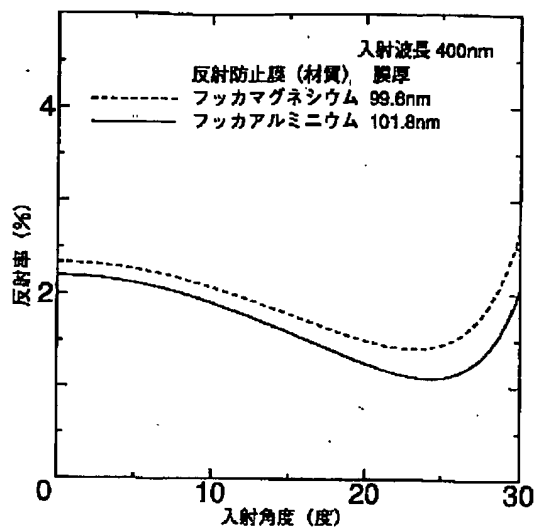
[Drawing 1]



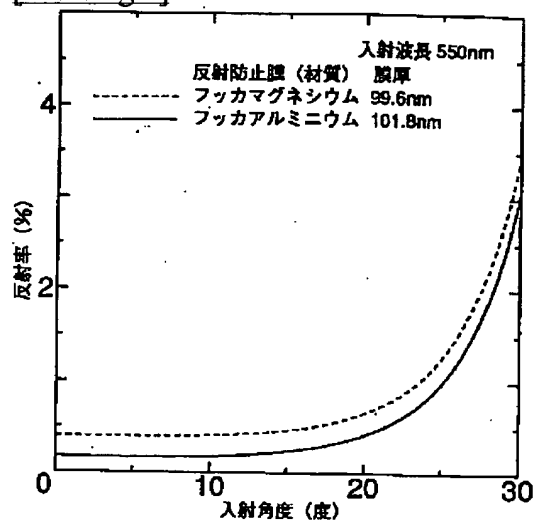
[Drawing 2]



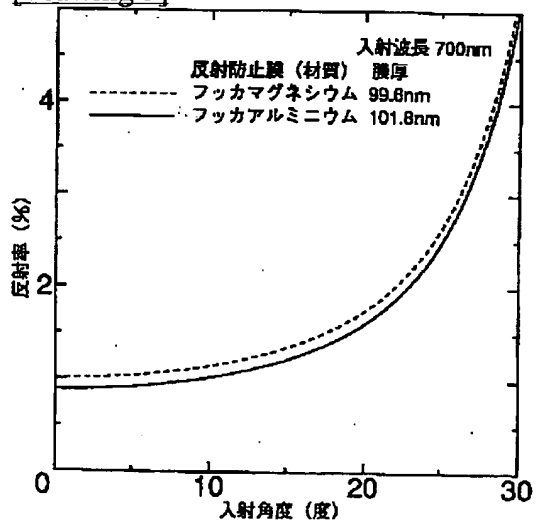
[Drawing 3]



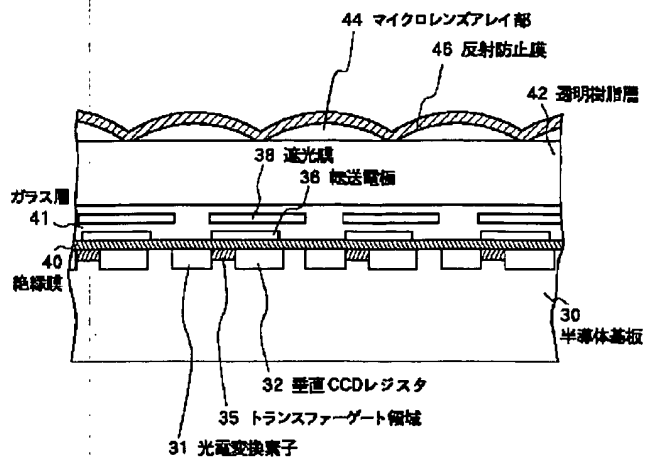
[Drawing 4]



[Drawing 5]



[Drawing 6]



[Translation done.]